

Calorimetric Evidence for a Fulde–Ferrell–Larkin–Ovchinnikov Superconducting State in the Layered Organic Superconductor κ -(BEDT-TTF)₂Cu(NCS)₂

R. Lortz,¹ Y. Wang,² A. Demuer,² P.H.M. Böttger,³ B. Bergk,³ G. Zwicknagl,⁴ Y. Nakazawa,⁵ and J. Wosnitzer³

¹*Department of Condensed Matter Physics, University of Geneva, CH-1211 Geneva 4, Switzerland*

²*Grenoble High Magnetic Field Laboratory, CNRS, 38042 Grenoble Cedex 9, France*

³*Hochfeld-Magnetlabor Dresden (HLD), Forschungszentrum Dresden-Rossendorf, D-01314 Dresden, Germany*

⁴*Institut für Mathematische Physik, Technische Universität Braunschweig, D-38106 Braunschweig, Germany*

⁵*Department of Chemistry, Osaka University, 1-1, Machikaneyama, Toyonaka, Osaka, Japan*

(Dated: February 1, 2008)

The specific heat of the layered organic superconductor κ -(BEDT-TTF)₂Cu(NCS)₂, where BEDT-TTF is bisethylenedithio-tetrathiafulvalene, has been studied in magnetic fields up to 28 T applied perpendicular and parallel to the superconducting layers. In parallel fields above 21 T, the superconducting transition becomes first order, which signals that the Pauli-limiting field is reached. Instead of saturating at this field value, the upper critical field increases sharply and a second first-order transition line appears within the superconducting phase. Our results give strong evidence that the phase, which separates the homogeneous superconducting state from the normal state is a realization of a Fulde-Ferrell-Larkin-Ovchinnikov state.

PACS numbers: 74.70.Kn, 75.40.Cx, 74.25.Bt, 65.40.Ba

The influence of high magnetic fields on the superconducting state is of high technological and fundamental relevance. Applied aspects such as high superconducting current densities as well as basic questions on the nature of the superconducting state are of special interest. In type-II spin-singlet superconductors, a magnetic field destroys superconductivity in two distinct ways: i.e., by orbital and Pauli-paramagnetic pair-breaking effects. In general, both effects limit the maximum upper critical field, H_{c2} , above which the normal-conducting state is restored. In most type-II superconductors the orbital effect plays the dominant role. If, however, under certain circumstances, the orbital pair-breaking field, H_{orb} , is clearly larger than the Pauli paramagnetic limit, H_P , the superconductor may enter a special, spatially modulated, superconducting state at high magnetic field and low temperatures. As predicted independently by Fulde and Ferrell [1] and Larkin and Ovchinnikov [2] in 1964, in this so-called FFLO (or LOFF) state superconductivity can survive even above the Pauli limit by “sacrificing” parts of the material volume to the normal state.

In the FFLO state, the Zeeman-split Fermi surfaces allow Cooper pairing only with a finite center-of-mass momentum \mathbf{q} resulting in an oscillating part of the order parameter in real space with wavelength of the order of the coherence length, ξ . For the FFLO state to occur the so-called Maki parameter [3], $\alpha = \sqrt{2}H_{orb}/H_P$, should be larger than 1.8 [4] and the superconductor needs to be in the clean limit with a mean-free path, ℓ , much larger than ξ . Not many superconductors fulfil these conditions and early searches failed to observe the FFLO state. In the 1990s, some reports claiming evidence for the FFLO state appeared that later had to be revised. For more details see [5] and the recent reviews [6, 7].

Only recently, solid thermodynamic evidence for the

existence of the FFLO state has been put forward for the heavy-fermion compound CeCoIn₅ [8, 9]. Besides heavy-fermion superconductors the quasi-two-dimensional (2D) organic superconductors have been suggested as good candidates for exhibiting the FFLO state [6, 7, 10, 11]. For these the orbital pair breaking can be greatly suppressed when applying the magnetic field parallel to the highly conducting layers [10, 11, 12]. Indeed some signs, but no thermodynamic proof, for an FFLO state in 2D organic superconductors have been reported [13, 14, 15]. For λ -(BETS)₂GaCl₄ a kink in the thermal conductivity [14] and for λ -(BETS)₂FeCl₄ dip structures in the resistance [15] suggested the existence of a FFLO state (BETS is bisethylenedithio-tetraselenafulvalene). For κ -(BEDT-TTF)₂Cu(NCS)₂ the existence of the FFLO phase had been inferred from measurements sensitive to a loss in vortex stiffness (BEDT-TTF is bisethylenedithio-tetrathiafulvalene) [13]. The observed features are, however, rather broad anomalies that do not fit with our specific-heat results discussed below and are, therefore, most probably not related to the FFLO state.

In this Letter, we present clear thermodynamic evidence that for κ -(BEDT-TTF)₂Cu(NCS)₂ a narrow intermediate superconducting state, most probably an FFLO state, evolves at high magnetic fields applied parallel to the layers. At this Pauli-limited field region the slope of the upper-critical-field line increases sharply and a first-order transition appears below H_{c2} .

Single crystals of κ -(BEDT-TTF)₂Cu(NCS)₂ were grown by the standard electrochemical-oxidation method as described elsewhere [16]. The specific heat was measured by use of a miniaturized relaxation technique [17, 18] in Geneva up to 14 T and in the Grenoble High Magnetic Field Laboratory up to 28 T. In both cases, the same calorimeter was used without removing the sam-

ple between the experiments. The chip resistance and the thermal conductance of the leads have been carefully calibrated up to 28 T using a capacitance thermometer. Each relaxation provides about 1000 data points over a temperature interval of 30-40% above the base temperature, which has been varied between 1.3 and 12 K. Data can be recorded during heating and cooling, which allows to resolve hysteresis effects close to first-order transitions. The merging of the upward and downward relaxation data provides a highly reliable check of the accuracy of this method.

The specific heat is a purely thermodynamic bulk quantity. Effects related to flux pinning or vortex instabilities can thus be excluded [19]. We precisely aligned the sample for parallel-field orientation by slightly turning the cryostat in the bore of the resistive coil while maximizing the superconducting transition temperature in an intermediate field of 8 T. We found that a good indicator for a perfect orientation was the absence of the first-order vortex-melting transition in fields between 3 and 14 T which is observable in slightly tilted fields [20].

In order to determine the particular band-structure parameters of the investigated specific-heat sample we measured the de Haas-van Alphen (dHvA) effect by use of the cantilever-torque technique in a ^3He cryostat.

The inset of Fig. 1(a) shows specific-heat data taken in 0 and 14 T applied perpendicular to the superconducting layers. The specific-heat anomaly, which represents only 5% of the total specific heat, is visible in zero field at $T_c = 9.1$ K. The curves merge for all fields between 4 and 14 T which indicates that the upper critical field is reached at about 4 T for this field orientation. The 14-T data thus represent the normal state and allow us to extract the Sommerfeld constant, γ , and to separate the phonon background. We obtain $\gamma = 26(2) \text{ mJmol}^{-1}\text{K}^{-2}$ and a Debye temperature of about 200 K. These values as well as the overall specific heat are in very good agreement with earlier results [21, 22, 23]. Subtraction of the phonon contribution, i.e., the 14-Tesla data minus γT , results in the electronic specific heat, C_e , shown for fields applied perpendicular and parallel to the layers in Fig. 1(a) and 1(b), respectively. From the size of the specific-heat jump $\Delta C = 0.58 \text{ Jmol}^{-1}\text{K}^{-2}$ we obtain the ratio $\Delta C/(\gamma T_c) = 2.5(2)$, which, in accordance with earlier reports [22, 23], is larger than the BCS value (1.43) and thus proves strong coupling.

The specific heats look rather different for the two field orientations. For perpendicular fields the superconducting transition is strongly broadened already in small fields due to fluctuations. This can be explained by a field-induced finite-size effect in layered superconductors [24]. Contrary to standard superconductors in which T_c is lowered in a field but essentially remains sharp, the onset of the transition in $\kappa\text{-(BEDT-TTF)}_2\text{Cu(NCS)}_2$ is hardly influenced. Instead, each sign of superconductivity continuously fades away while reaching H_{c2} . A

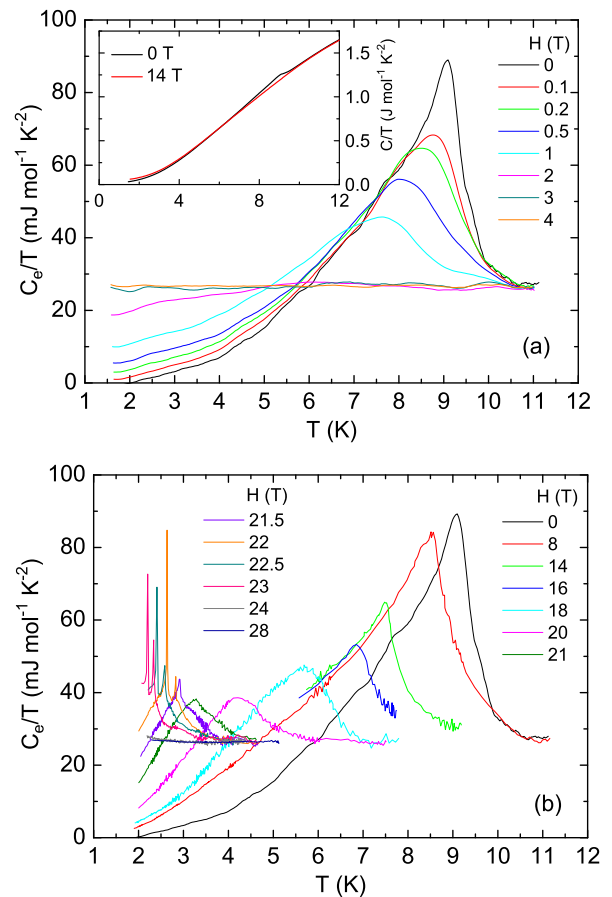


FIG. 1: (color) Temperature dependence of the electronic contribution to the specific heat, C_e/T , of $\kappa\text{-(BEDT-TTF)}_2\text{Cu(NCS)}_2$ in magnetic fields applied perpendicular (a) parallel (b) to the superconducting layers. Data taken in 14 T applied perpendicular to the layers (inset) were used to separate the phonon contribution.

possible scenario may therefore be that in $\kappa\text{-(BEDT-TTF)}_2\text{Cu(NCS)}_2$ only the phase coherence is lost in magnetic fields, while Cooper pairs still exist above H_{c2} .

For fields applied parallel to the layers we find as well a broadening of the superconducting transition, but this effect is less pronounced and a clear shift of the specific-heat anomaly occurs. This resembles more a standard behavior. The effect of fluctuations is nevertheless also visible for this field orientation.

Above ~ 14 T, T_c shifts rather rapidly with increasing field and the transition becomes strongly broadened by fluctuations. At about 21 T, the anomaly in C sharpens and at 21.5 T a spike in C due to the latent heat of a first-order transition appears (Fig. 2). For higher fields up to 23 T, two sharp anomalies in C clearly prove the existence of an additional thermodynamic phase within the superconducting state. The lower transition shows a well-resolvable temperature hysteresis (~ 0.05 K at 22 T), while the main superconducting transition develops only

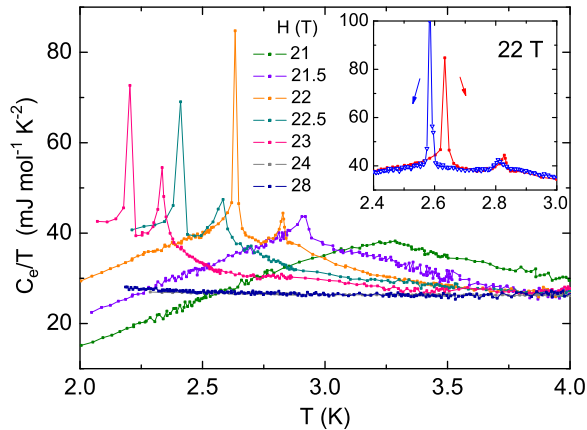


FIG. 2: (color) Details of C_e/T of κ -(BEDT-TTF) $_2$ Cu(NCS) $_2$ in high magnetic fields applied parallel to the superconducting layers.

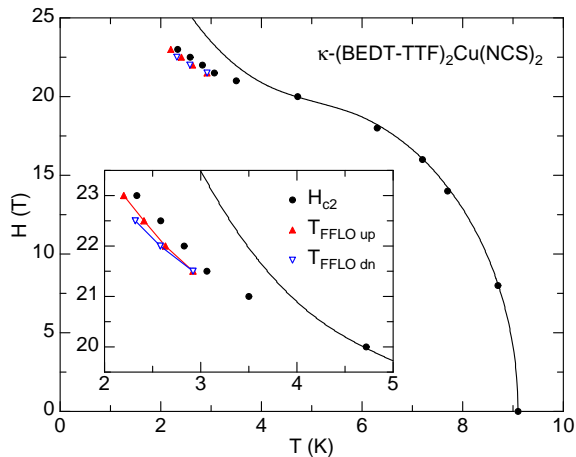


FIG. 3: (color) Phase diagram of κ -(BEDT-TTF) $_2$ Cu(NCS) $_2$ for fields applied parallel to the superconducting layers. The solid line represents the calculated H_{c2} using the known band-structure parameters. See the text for details.

a small hysteresis < 0.02 K (inset of Fig. 2). We were able to follow the two transitions up to 23 T, above which they left the temperature window of our experiment.

The extracted magnetic phase diagram with H_{c2} and the second transition including its hysteresis is shown in Fig. 3. At high temperatures, H_{c2} increases very steeply, before it levels off towards saturation at lower T . This clearly signals the crossover from an orbital T_c reduction at low fields towards a Pauli-paramagnetic limitation at higher fields. From the initial critical-field slope, $H'_{c2} = dH_{c2}/dT$, the orbital-limiting field, H_{orb} , can be estimated. Using the T_c reduction of about 0.4 K at 8 T, i.e., $H'_{c2} = 20$ T/K, we obtain $H_{orb} = 0.7H'_{c2}T_c \approx 130$ T, much larger than the low-temperature H_{c2} we observe.

The large value of H_{orb} results from the strongly reduced orbital currents for the field orientation parallel

to the layers. For that reason the field-induced spin polarization becomes important resulting in the rapid T_c reduction. For κ -(BEDT-TTF) $_2$ Cu(NCS) $_2$, the Pauli-limiting field can be determined quite accurately from $H_P = \Delta_0/(\sqrt{2}\mu_B)$ [25], where μ_B is the Bohr magneton and the superconducting energy gap, Δ_0 , is well known from specific-heat studies [22, 23]. Using $\Delta_0/k_B T_c = 2.4$ [23], we obtain $H_P = 23$ T which agrees very well with the observed limitation of H_{c2} towards low temperatures (Fig. 3). Indeed, the crossover of the broadened superconducting transition to a sharp first-order transition shows that the Pauli-limiting field is reached at ~ 21 T.

Above this field, the H_{c2} line clearly increases its slope and the transition develops a latent heat. Simultaneously, the second transition line appears within the superconducting phase. This strongly suggests the evolution of the FFLO state in κ -(BEDT-TTF) $_2$ Cu(NCS) $_2$. Indeed, this superconductor fulfils all requirements necessary for the formation of the FFLO state. First, it is a strongly type-II superconductor with a large Ginzburg-Landau parameter κ of 100 – 200 even for perpendicular fields [26]. Second, the Maki parameter, $\alpha = \sqrt{2}H_{orb}/H_P \approx 8$ is more than four times larger than required [4]. Finally, ξ is much smaller than the mean-free path, ℓ . The latter was determined for the investigated sample by means of dHvA measurements. In accordance with well established literature data [27], two dHvA frequencies were resolved. The lower frequency, $F_\alpha = 600(1)$ T, originating from a hole orbit, together with the measured effective mass, $m_c^\alpha = 3.05(10)m_e$, allows to calculate the Fermi energy $\epsilon_F^\alpha = 23$ meV, where m_e is the free-electron mass. For the larger breakdown orbit [$F_\beta = 3870(20)$ T, $m_c^\beta = 6.5(2)m_e$], comprising all electrons at the Fermi level, the Fermi energy is $\epsilon_F^\beta = 69$ meV. The field dependence of the dHvA amplitude gives the scattering time $\tau = 1.9 \times 10^{-12}$ s for the α orbit. The magnetic breakdown allows the determination of the scattering time for the β orbit only with much larger error bars. Assuming an unchanged τ leads to $\ell = 100$ and 115 nm, respectively. By use of $H_{c2\perp} = 4$ T from our specific-heat data [Fig. 1(a)], $\xi \approx 9$ nm. Correspondingly, $\ell/\xi \approx 12$ proves that our sample is in the clean limit.

We may now compare our results with the calculated phase diagram for magnetic fields parallel to the layers. For that, we assume s -wave superconductivity [22, 23, 28], although that is not an essential ingredient. Detailed studies [11, 12] showed that the transition lines, the orders of the transitions, and the structures of the equilibrium states depend very sensitively on the electronic structure, i.e., on the Fermi surface, the effective masses of the quasiparticles, and their interactions. We model the system under consideration by a stack of 2D superconducting planes with negligibly small conductivity perpendicular to the planes and use the Fermi surface and effective masses derived from the dHvA experiments. As the magnetic susceptibil-

ity in the normal state is not significantly renormalized compared to the expected value for free quasiparticles we neglect Landau's spin-dependent interaction parameter F_0^a . For a quantitative comparison with experiment we have to account for corrections due to the strong electron-phonon coupling. Considering the rather small ratio $(k_B T_c)/(\hbar \langle \omega \rangle) \simeq 0.08$ [29] we anticipate neither pronounced anomalies in the variation with T of the enhancement factors nor significant differences in critical-field renormalizations corresponding to first and second-order transitions, respectively [30]. As we are mainly interested in the low- T behavior we implicitly account for strong-coupling corrections by rescaling the weak-coupling results with the enhancement factor for the low- T energy gap $\Delta_0/(1.76 k_B T_c) \simeq 1.35$ [23]. The solid line in Fig. 3 displays the resulting critical field for the second-order transition from the normal to the inhomogeneous FFLO state which agrees well with experiment. The anisotropy of the effective masses which differ by a factor of ~ 2 on the different Fermi-surface sheets stabilizes the inhomogeneous superconducting state and leads to the steep upturn in $H_{c2}(T)$. Following Ref. [31] we find that the transition is of second order in the vicinity of the tricritical point in close analogy to the case of the isotropic 2D superconductor with non-interacting quasiparticles. For a better description of the low- T $H_{c2}(T)$ data and for estimating the transition from the homogeneous superconducting to the FFLO state more detailed information on the electronic parameters is necessary.

When we compare the phase diagram in Fig. 3 with that of CeCoIn₅ [5] we find clear qualitative differences. For CeCoIn₅, H_{c2} is less reduced at high fields due to Pauli limitation and there is no clear upturn of H_{c2} when the FFLO state appears. The latter may be due to the rather isotropic in-plane effective masses. For the 2D organic material, the FFLO phase occupies only a small area in the phase diagram with the transition line following closely the H_{c2} transition (Fig. 3). Another difference is found in the nature of the transitions. For the organic superconductor both transitions are found to be first order, whereas for CeCoIn₅ only the H_{c2} line is first order. Both materials have similar values for α and ℓ/ξ (see [32] for recent estimates). A possible reason for these differences might be the anisotropy which for CeCoIn₅ is much smaller than for κ -(BEDT-TTF)₂Cu(NCS)₂. For the latter the ratio of the Fermi energy with respect to the interlayer hopping, ϵ_F/t_\perp , is about 3700 [33]. Finally, we see no evidence for an FFLO state in the field perpendicular orientation, whereas for CeCoIn₅ the matter is still unresolved [5, 8, 9].

In conclusion, we presented high-resolution specific-heat data in high magnetic fields that give clear thermodynamic evidence for the existence of a narrow additional superconducting phase in the 2D organic superconductor κ -(BEDT-TTF)₂Cu(NCS)₂ for in-plane magnetic fields. This phase is most probably a realization of the long-

time predicted FFLO state. This is supported by the paramagnetic limitation of H_{c2} , the upturn of H_{c2} when the Pauli-limiting field of 21.5 T is reached, and the first-order nature of the transitions above this field. The clear observation of the FFLO state in a second superconductor, besides CeCoIn₅, with a qualitative different phase diagram allows for thorough tests of our fundamental understanding of superconductivity at high magnetic fields.

We thank A. Junod, P. Fulde, A.D. Bianchi, T. Giamarchi, Ø. Fisher, and C. Berthier for stimulating discussions and S. Debrion, I. Sheikin, T.T. Lortz, and the technicians of the Grenoble High Field Laboratory for their experimental support.

-
- [1] P. Fulde and R.A. Ferrell, Phys. Rev. **135**, A550 (1964).
 - [2] A.I. Larkin and Y.N. Ovchinnikov, Zh. Eksp. Teor. Fiz. **47**, 1136 (1964) [Sov. Phys. JETP **20**, 762 (1965)].
 - [3] K. Maki and T. Tsuneto, Prog. Theor. Phys. **31**, 945 (1964).
 - [4] L.W. Gruenberg and L. Gunther, Phys. Rev. Lett. **16**, 996 (1966).
 - [5] A. Bianchi *et al.*, Phys. Rev. Lett. **89**, 137002 (2002).
 - [6] R. Casalbuoni and G. Nardulli, Rev. Mod. Phys. **76**, 263 (2004).
 - [7] Y. Matsuda and H. Shimahara, J. Phys. Soc. Jpn. **76**, 051005 (2007).
 - [8] A. Bianchi *et al.*, Phys. Rev. Lett. **91**, 187004 (2003).
 - [9] H.A. Radovan *et al.*, Nature **425**, 51 (2003).
 - [10] H. Shimahara, Phys. Rev. B **50**, 12 760 (1994).
 - [11] H. Shimahara, J. Phys. Soc. Jpn. **66**, 541 (1997).
 - [12] H. Burkhardt and D. Rainer, Ann. Phys. **506**, 181 (1994).
 - [13] J. Singleton *et al.*, J. Phys.: Condens. Matter **12**, L641 (2000).
 - [14] M.A. Tanatar *et al.*, Phys. Rev. B **66**, 134503 (2002).
 - [15] S. Uji *et al.*, Phys. Rev. Lett. **97**, 157001 (2006).
 - [16] H. Urayama *et al.*, Chem. Lett. **1988**, 55 (1988).
 - [17] F. Bouquet *et al.*, Phys. Rev. Lett. **89**, 257001 (2002).
 - [18] E. van Heumen *et al.*, Phys. Rev. B **75**, 054522 (2007).
 - [19] R. Lortz *et al.*, Phys. Rev. B **75**, 094503 (2007).
 - [20] R. Lortz, unpublished.
 - [21] B. Andraka *et al.*, Phys. Rev. B **40**, 11 345 (1989).
 - [22] J. Müller *et al.*, Phys. Rev. B **65**, 140509 (2002).
 - [23] J. Wosnitza *et al.*, Synth. Met. **133-134**, 201 (2003).
 - [24] R. Lortz *et al.*, Phys. Rev. Lett. **91**, 207001 (2003).
 - [25] A.M. Clogston, Phys. Rev. Lett. **9**, 266 (1962).
 - [26] M. Lang and J. Müller, in *The Physics of Superconductors* Vol. II, ed. by K.H. Bennemann and J.B. Ketterson (Springer, Berlin, 2004), p. 453.
 - [27] J. Wosnitza, *Fermi Surfaces of Low-Dimensional Organic Metals and Superconductors* (Springer, Berlin, 1996).
 - [28] H. Elsinger *et al.*, Phys. Rev. Lett. **84**, 6098 (2000).
 - [29] J. Hagel *et al.*, Phys. Rev. B **68**, 104504 (2003).
 - [30] D. Rainer and G. Bergmann, J. Low Temp. Phys. **14**, 501 (1974).
 - [31] R. Combescot and C. Mora, Eur. Phys. J. B **28**, 397 (2002).
 - [32] C.F. Miclea *et al.*, Phys. Rev. Lett. **96**, 117001 (2006).
 - [33] J. Singleton and C. Mielke, Contemp. Phys. **43**, 63 (2002).